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EVALUATION OF SULPHOGYPSUM SAMPLES FROM VARENNES, QUEBEC, FOR GYPSUM PRODUCTS MANUFACTURE

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EVALUATION OF SULPHOGYPSUM SAMPLES FROM VARENNES,
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by

R.K. Collings* and G.A. Brown**

SUMMARY

Representative samples of sulphogypsum, which had been produced experimentally at Varennes, Quebec, by limestone neutralization of spent sulphuric acid effluent, were investigated in CANMET laboratories as raw material for gypsum products manufacture. Samples were calcined to the hemi-hydrate or plaster of Paris stage and the resulting products evaluated for time of set, strength, and bond to gypsum wallboard paper. Results indicated that a satisfactory product could be manufactured from this material. The sulphogypsum was well crystallized and, partly because of this, tended to be 'heavy' in the gypsum calcining kettle. Also, plaster of Paris-water mixtures tended to be 'stiff' during mixing and pouring. Both conditions were improved markedly by grinding prior to calcining. Plaster-water mixtures were quick setting but time of set was easily controlled with small additions of commercial retarder. The set plaster was of high strength. Bond of the plaster to gypsum wallboard paper unfortunately was poor. Bond was improved substantially by the addition of small quantities of starch to the plaster of Paris-water mixtures.

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INTRODUCTION

The sulphate process for the manufacture of titanium dioxide pigment results in a large quantity of spent sulphuric acid which constitutes a major disposal problem. Disposal by discharge into available water systems has been a common practice, however, concern regarding possible water pollution and resulting degradation of these systems has stimulated research and study by the titanium pigment industry of other, more acceptable disposal methods. One such method is neutralization of the acid with finely divided limestone and land storage or disposal of the resulting gypsum. The gypsum thus produced, because of its origin, commonly is referred to as 'sulphogypsum'. CANMET, the Canada Centre for Mineral and Energy Technology, has studied sulphogypsum produced experimentally in Quebec as potential raw material for gypsum products manufacture as part of a larger investigation of other types of synthetic gypsums available in Canada. This report summarizes laboratory research undertaken on sulphogypsum samples obtained from Canadian Titanium Pigments Limited, Varennes, Quebec.

SOURCE AND DESCRIPTION OF SAMPLES

Two sulphogypsum samples were examined. A 30 kg sample from early pilot-plant studies of the neutralization of spent sulphuric acid with limestone, obtained by the author during a visit to the Varennes plant in April, 1977, and a 330 kg sample from pilot-plant trials conducted at Varennes during the

summer of 1977. This latter sample was submitted at CANMET's request. Both samples were white to grey-white, finely divided and contained in excess of 92% gypsum. The laboratory study was restricted to the larger sample which was considered to be more representative of the material that could be produced at Varennes. This sample was finely divided and essentially minus 212 μm (70 mesh) in size as shown in Table 1. The pH was 4.5. A mineralogical analysis* showed this material to be principally gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with traces of bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and quartz. The gypsum content, based on combined water, was 92.6%, as noted in Table 2. This gypsum was well crystallized as shown by the photomicrographs, Figure 1.

TABLE 1
Sieve Analyses — Wt Per Cent

Size μm	Head Sample			
	As Rec'd	Calcined	Ground	Ground and Calcined
+600	1.1	-	-	-
-600 +425	0.6	-	0.1	-
-425 +212	1.7	-	0.3	0.2
-212 +150	4.5	.5	2.8	1.3
-150 +106	12.4	10.2	9.2	13.6
-106 + 75	16.7	4.0	9.6	21.7
- 75 + 45	15.5	27.5	13.9	11.2
- 45	48.5	57.8	64.1	52.0
Total	100.0	100.0	100.0	100.0

*Mineralogical analysis and photomicrographs (Figure 1) were by R.M. Buchanan, Ore Mineralogy Section.

TABLE 2

Chemical Analyses — Wt Per Cent⁽¹⁾

Compound	Head Sample	Chemically Pure Gypsum	Calculated ⁽²⁾ Gypsum Content
CaO	32.6	32.5	100.4
SO ₃	47.2	46.6	101.3
H ₂ O	19.4	20.9	92.6

- (1) Analyses by Chemical Laboratory, CANMET.
- (2) Based on CaO, SO₃ and H₂O contents, respectively, and as compared with chemically pure gypsum. The first two values, based on CaO and SO₃, appear to be too high, probably because of the presence of small quantities of unreacted limestone and sulphuric acid.



Mag 70X - Transmitted Light



Mag 70X - Crossed Polaroids

Figure 1. Gypsum Photomicrographs

LABORATORY STUDY

A sample of the sulphogypsum, as received, was calcined in a 25-kg capacity, gypsum calcining kettle (Cole). Unfortunately the full capacity of the kettle could not be utilized due to high internal friction within the sample which caused the driving motor for the mixing blades to stall when more than 19 kg of material was added. The 19 kg sample was calcined to a maximum temperature of 150°C over a 195 min period at an average temperature of 112°C (Sample A, Figure 2). Following calcining the product was screened on a 236 μ m (8 mesh) sieve, cooled and sealed in polyethylene bags. The calcined product was then evaluated for consistency, time of set, compressive strength and bond to gypsum wallboard paper as per CSA A82.20, Method of Testing Gypsum and Gypsum Products. Distilled water at room temperature (20°C), ASTM C-190 standard sand, and commercial retarder were used in all tests. The retarder was mixed with the water before addition of the plaster of Paris which was first screened through a 600 μ m (30 mesh) sieve. The water-plaster mixture was allowed to soak for 1 min prior to a 2 min period of mechanical mixing in a Hobart unit before testing. Preliminary tests were required to determine consistency and optimum time of set for placing the plaster in 50 mm (2 in.) cube gang moulds for compressive strength tests.

Data for the series of tests made on the as received sulphogypsum sample, Sample A, are recorded in Table 3, Gypsum Calcining Test Data, and in Table 4, Gypsum Plaster Test Data. An examination of this data reveals a number of interesting

points. Calcining produces an increase in surface area, and, of course, a decrease in combined water content; approximately 65 ml of water per 100 g of plaster of Paris were required to produce a workable (pourable) mix; the plaster of Paris was quick-set, 7 to 8 min, without retarder addition but of high strength; bond to gypsum wallboard paper was poor even with the addition of starch as a bonding agent. The sanded gypsum plaster samples were similarly quick setting without retarder addition, and of high strength.

Samples of the plaster of Paris were ground in a pebble mill to 150 μ m (100 mesh) in an attempt to improve bond to gypsum wallboard paper. Grinding produced some improvement in the bonding characteristics of this material as noted in Table 4.

A second calcining test was made in the gypsum kettle using pebble mill ground sulphogypsum (150 μ m) to determine whether pregrinding would result in improved performance in the kettle and in the bond of the calcined product to gypsum wallboard paper. The time-temperature calcining curve for this sample, Sample B, is similar to that for Sample A as noted in Figure 2. The plaster of Paris made from the preground gypsum, when mixed with water, was generally more workable than that made from the unground material. Data for Sample B are recorded in Tables 3 and 5. An examination of this data shows a 20% increase in the quantity of gypsum that could be fed to the kettle as a result of grinding to 150 μ m (100 mesh). Bond of the plaster-water slurry to gypsum wallboard paper was

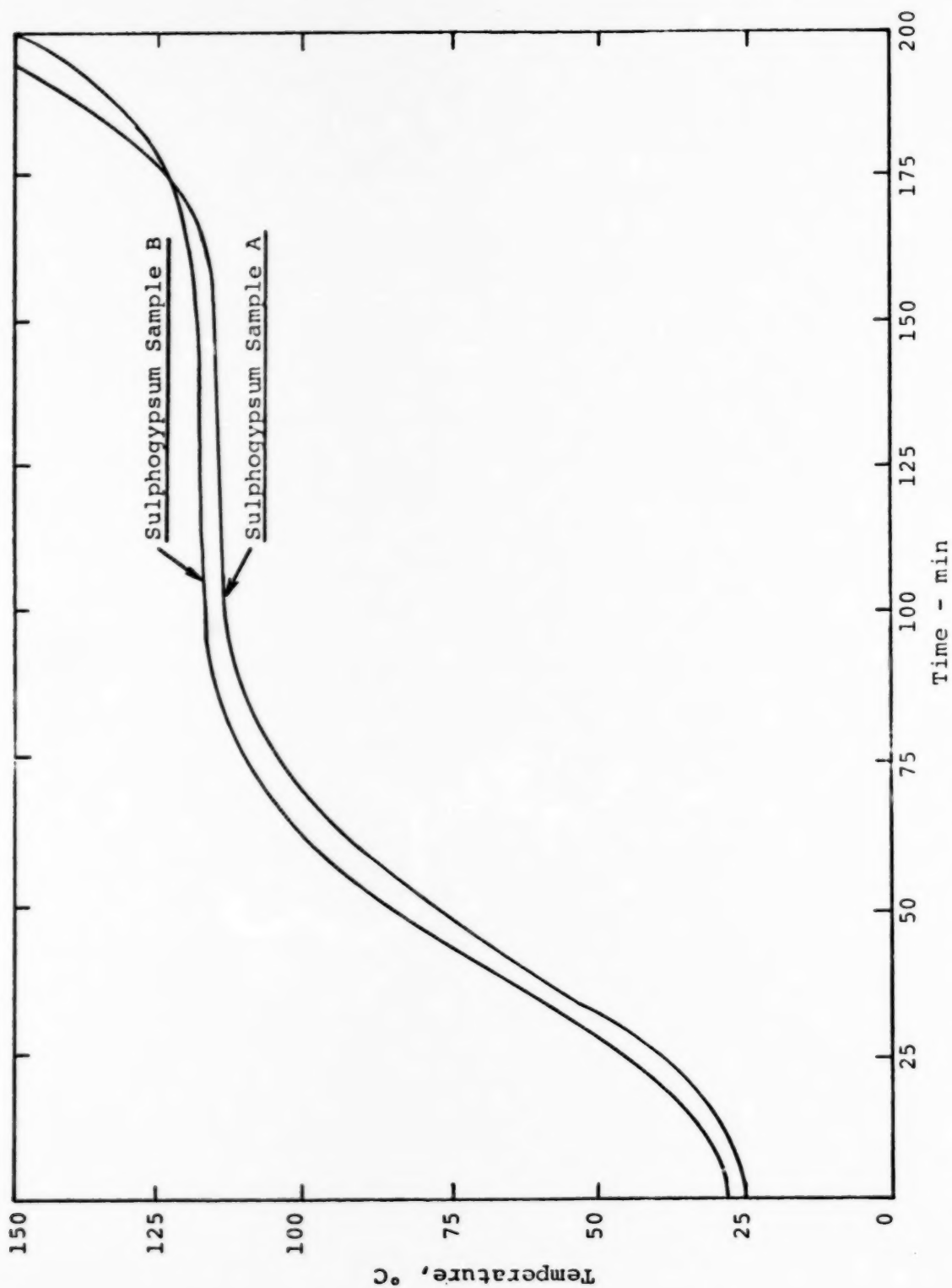


Figure 2. Time-temperature calcining curves, sulphogypsum samples A and B

TABLE 3
Gypsum Calcining Test Data — Sulphogypsum Samples A and B

Sample	Gypsum Kettle Feed				Calcining Cycle		Remarks
	Wt. (kg)	Surf. Area (cm ² /g)	pH	Comb. H ₂ O (wt %)	Time (min)	Max. Temp. (°C)	
A (head sample - as rec'd)	19	2025 (93% minus 150 μ m)	4.5	19.4	195	150	Calcined in 25-kg capacity Cole gypsum calcining kettle; quantity calcined, 19 kg, was less than optimum charge because further addition caused driving motor for mixing blades to stall; grinding before calcining probably would overcome this problem by reducing internal friction in the gypsum sample.
B (head sample - ground in pebble mill)	23	4025 (97% minus 150 μ m)	4.7	19.4	200	150	Calcined in Cole kettle; charge to kettle was only 23 kg which was the amount of material available; additional material undoubtedly could have been added without stalling the driving motor; grinding increased surface area by 100%.

(1) Surface area, Blaine air permeability apparatus.

TABLE 4

Gypsum Plaster Test Data — Sample A

Sample A	Plaster of Paris			Additives			Set Plaster				Remarks		
	Wt (g)	Surf. Area (cm ² /g)	Comb. H ₂ O (wt %)	Water (ml)	Sand (g)	Retard (g)	Starch (g)	Time of Set (min)	Dens. (g/cc)	Comp. Str (MPa)		Bond to Paper Ivory Grey	
Plaster of Paris		5040	4.7										
Prel. tests	100			65	-	-	-	7			-	-	
	100			65	-	0.1	-	26			poor	poor	
	100			65	-	0.1	1.0	25			poor	poor	
	100	ground to minus 150 µm		65	-	0.1	1.0	24.5			fair	good	
Compressive strength tests	1200			780	-	1.2	-	23.5	1.14	13.8 (1998 psi)			
Plaster of Paris and Sand													
Prel. tests	50			45	150	-		8.5	-	-			
	50			45	150	0.05		22.5	-	-			
Compressive strength tests	750			625	1500	0.75		20.0	1.56	7.9 (1150 psi)			
											Plaster-sand mixture is quick-set but set is easily extended with commercial retarder; compressive strength of plaster-sand mixture, at 7.9 MPa, is well above the CSA, A82 requirement of 5.2 MPa.		

(1) Surface area, Blaine air permeability apparatus.

TABLE 5

Gypsum Plaster Test Data - Sample B

Sample B	Plaster of Paris			Additives			Plaster			Remarks			
	Wt (g)	Surf. Area (cm ² /g)	pH	Comb. H ₂ O (wt %)	Water (ml)	Sand (g)	Retard. (g)	Starch (g)	Time of Set (min)		Dens. (g/cc)	Comp. Str. (MPa)	Bond to Paper Ivory
Plaster of Paris		5000	4.8	6.5									
Prel. tests	100				65	-	-	-	13				
	100				65	-	0.1	-	20			poor	
	100				65	-	0.1	0.1	22			fair	good
Compressive strength tests	1200				780	-	1.2	-	6		16.7		
	1200				780	-	2.0	-	13		12.3 (1785 psi)		
Plaster of Paris and Sand													
Prel. tests	50				45	150	-		8.5				
	50				45	150	0.1		24.0				
Compressive strength tests	750				625	1500	0.75		7.0		7.5		
	750				625	1500	1.50		25.0		7.3 (1060 psi)		
Surface area of plaster of Paris prepared from B is similar to that prepared from A despite pregrinding of B; acid nature of plaster B is evident as for A; grinding appears to have extended time of set somewhat; bond to paper continues to be poor despite pregrinding but is improved by starch addition; calculated quality of retarder for compressive strength tests, 0.1%, was too low and resulted in thick and quick-set plaster; with increased retarder, 0.2%, a more workable, slower setting plaster of somewhat lower strength was produced.													
Plaster-sand mixture without retarder is quick-set; as above, the calculated quantity of retarder for compressive strength tests was too low and had to be doubled to produce a free-flowing, workable mix; compressive strength, at 7.3 MPa, exceeds CSA A82 requirement of 5.2 MPa.													

(1) Surface area, Blaine air permeability apparatus.

generally poor and not markedly improved by fine grinding. The addition of 1% starch improved the bond, especially with the grey, backing paper. Time of set and compressive strengths of the unground and ground samples were comparable.

The rapid set of unretarded gypsum plaster Samples A and B is attributable in part to the low pH, 4.7 to 4.8. Acid plasters normally are rapid setting. Neutralization with an appropriate base, e.g., calcium hydroxide, could be employed to delay the setting action. However, set control was easily achieved in these experiments by the use of small quantities of commercial retarder.

CONCLUSIONS AND RECOMMENDATIONS

Based on the samples received and the results of this present study, sulphogypsum from pilot-plant trials at Varennes, Quebec, is technically suitable as raw material for gypsum plaster manufacture. Grinding prior to calcining is recommended, however, to maximize the charge to the calcining kettle and to improve product workability and quality. Further studies, including neutralizing of the slightly acid plaster of Paris to produce a slower setting and more acceptable product, and studies directed towards improving the bond of the plaster to gypsum wallboard paper, are recommended.

POOR

QUALITY

ORIGINAL